

Thermochemistry and Hess's Law

In this experiment you will determine the enthalpy change that occurs when sodium hydroxide and hydrochloric acid solutions are mixed. Next, the enthalpy change for the reaction between sodium hydroxide and ammonium chloride will be measured. Lastly, you will determine the enthalpy change for the reaction between ammonia and hydrochloric acid. An algebraic combination of the first two equations can lead to the third equation. Therefore, according to Hess's law, an algebraic combination of the enthalpy changes of the first two should lead to the enthalpy of the third reaction.

The molecular equations for the reactions are as follows:

- (1) $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
- (2) $\text{NH}_4\text{Cl(aq)} + \text{NaOH(aq)} \rightarrow \text{NH}_3\text{(aq)} + \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
- (3) $\text{NH}_3\text{(aq)} + \text{HCl(aq)} \rightarrow \text{NH}_4\text{Cl(aq)}$

There is no single instrument that can directly measure heat in the way a balance measures mass or a thermometer measures temperature. However, it is possible to determine the heat change when a chemical reaction occurs. The change in heat is calculated from the mass, temperature change, and specific heat of the substance which gains or loses heat.

The equation that is used to calculate heat gain or loss is:

$$q = (\text{grams of substance}) \times (\text{specific heat}) \times \Delta T$$

where q = the heat energy gained or lost and ΔT is the change in temperature. Since ΔT = (final temperature minus initial temperature), an increase in temperature will result in a positive value for both ΔT and q , and a loss of heat will give a negative value. A positive value for q means a heat gain, while a negative value means a heat loss.

Acid-base neutralization is an exothermic process. Combining solutions containing an acid and a base results in a rise of solution temperature. The heat given off by the reaction (which will cause the solution temperature to rise) can be calculated from the specific heat of the solution, the mass of solution and the temperature change. This heat quantity can then be converted to the enthalpy change for the reaction in terms of kJ/mole by using the concentrations of the reactants.

According to Hess, if a reaction can be carried out in a series of steps, the sum of the enthalpies for each step should equal the enthalpy change for the total reaction. Another way of stating "Hess's Law" is: If two chemical equations can algebraically be combined to give a third equation, the values of ΔH for the two equations can be combined in the same manner to give ΔH for the third equation. An examination of the acid-base equations above shows that if equation (2) is subtracted from equation (1), equation (3) will result. Therefore, if the value of ΔH for equation (2) is subtracted from that of equation (1), the enthalpy change for equation (3) should result. We will test this idea in this experiment.

Chemicals

Hydrochloric acid, HCl, 2.0 M

Ammonia, NH_3 , 2.0 M

Baking soda, $\text{NaHCO}_3\text{(s)}$,

Sodium hydroxide, NaOH, 2.0 M

Ammonium chloride, NH_4Cl , 2.0 M

Vinegar, $\text{HC}_2\text{H}_3\text{O}_2\text{(aq)}$

Equipment

Graduated cylinder, 25- or 50-mL

Beaker

Calorimeter made of two nested Styrofoam® Cups
and a cover

Fume hood

Magnetic stirrer and stirring bar (optional)

Ring stand, ring, wire gauze, Bunsen burner

Thermometer (preferably one that is
calibrated $\pm 0.1^{\circ}\text{C}$)

Procedure

Safety Alert

You will be working with strong acids and bases in concentrated solutions. The ammonia and hydrochloric acid have strong odors. If you spill any on yourself, wash off with lots of water. Neutralize acid spills on the lab bench with baking soda. Neutralize ammonia and sodium hydroxide spills with vinegar, which is dilute acetic acid.

Wear Chemical Splash Goggles and a Chemical-Resistant Apron.

1. Find the Heat Capacity of the Calorimeter.

Construct a calorimeter of two nested Styrofoam cups with a cover which has a hole in it to accept a thermometer. Measure 50.0 mL of distilled water at room temperature into the calorimeter. Place the assembly on a magnetic stirring motor, add a magnet and turn on the motor so the stirring bar spins slowly. (Alternatively, gently stir the solution with your thermometer.) Now record the temperature as precisely as you can.

Heat about 75 mL of distilled water to about 70°C . Measure 50.0 mL of this water into a different Styrofoam cup and precisely record its temperature. Immediately pour the hot water into the room temperature water, cover, insert the thermometer, stir and record the temperature every 20 seconds for three minutes.

2. Find the Heat of the Reactions.

Determine the temperature change that occurs when 50.0 mL of 2.0 M HCl solution reacts with 50.0 mL of 2.0 M NaOH. First, measure the temperature of each of the solutions. Be sure to rinse and dry the thermometer before transferring it to a second solution. The solution temperatures should agree $\pm 0.2^{\circ}\text{C}$. If they do not agree, you should use the average temperature as your initial temperature.

Measure out 50.0 mL of 2.0 M HCl and put it in the calorimeter. Put a stirring magnet in the solution, and set it moving gently (or stir gently with your thermometer). Measure out 50.0 mL of 2.0 M NaOH, add it to the acid, quickly cover and insert the thermometer. Record the temperature to the nearest 0.1°C after 20 seconds, and every 20 seconds for 3 minutes.

Safety Alert

When NaOH and NH_4Cl solutions are mixed, ammonia gas is evolved. Work in a hood or under a funnel attached to an aspirator.

Repeat the procedure, combining solutions of 2.0 M NH_4Cl and 2.0 M NaOH , and for the third reaction combining solutions of 2.0 M NH_3 and 2.0 M HCl . Be sure that containers and thermometers are rinsed and dried between reactions.

Calculations

1. Calculate the Heat Capacity of the Calorimeter.

- a. When equal volumes of hot and cold water are combined, if there is no heat loss the new temperature should be the average of the two starting temperatures. In actual practice, the new temperature will be slightly less than the average because of heat lost to the calorimeter assembly.

Additionally, when two solutions are mixed the thermometer cannot instantaneously record the temperature of the combined solutions. The solutions require some time to become completely mixed, and the thermometer needs time to come to temperature equilibrium with the solution. The theoretical temperature that the mixture would have if the process occurred instantaneously can be found from a graph.

Plot the data with temperature on the vertical axis versus time on the horizontal axis. The first few points may be erratic because of incomplete mixing and lack of temperature equilibrium with the thermometer. The points that follow should occur in a straight line as the temperature slowly drops while heat is lost to the calorimeter and to the surroundings. Draw a straight line through these points, and extend it back to find the temperature at time zero, the theoretical instantaneous temperature of mixing, T_{mix} . See Figure 1.

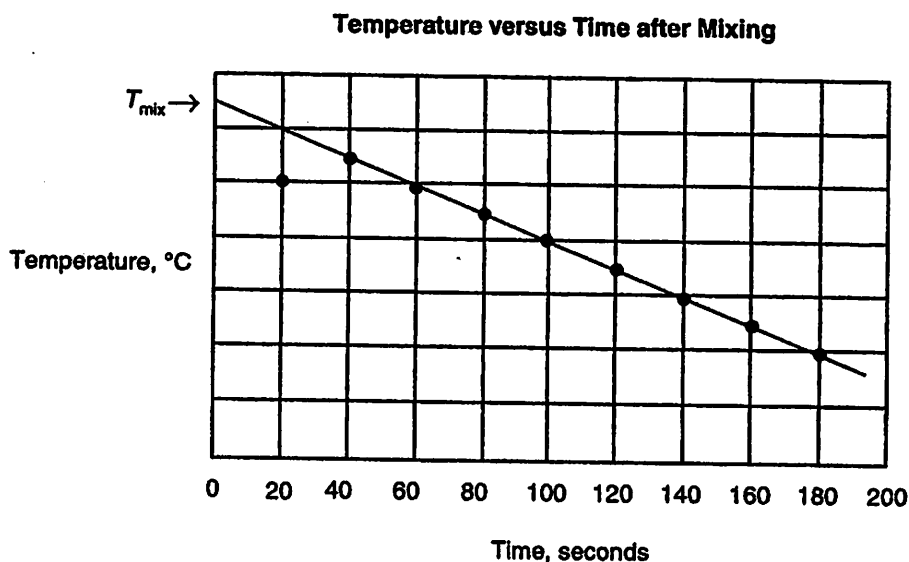


Figure 1. Graph to Find Heat Capacity of Calorimeter

- b. Calculate the average temperature of the hot and cold water, T_{avg} .
- c. The difference between the average temperature, T_{avg} and the instantaneous temperature, T_{mix} , is due to the fact that some heat was lost by the water and absorbed by the calorimeter. Calculate q_{water} , the heat lost by the water:

$$q_{\text{water}} = (\text{grams of water}) \times (\text{specific heat of water}) \times (T_{\text{mix}} - T_{\text{avg}})$$

where q_{water} = heat lost by water and the specific heat of water is $4.18 \text{ J/(g}\cdot\text{°C)}$.

The heat absorbed by the calorimeter, $q_{\text{calorimeter}}$, will be equal to that lost by the water but opposite in sign.

$$q_{\text{calorimeter}} = -q_{\text{water}}$$

- d. Calculate the heat capacity of the calorimeter, $C_{\text{calorimeter}}$, which is the heat that the calorimeter absorbs each time the temperature of the solution changes 1°C :

$$C_{\text{calorimeter}} = q_{\text{water}} / (T_{\text{mix}} - T_{\text{initial}})$$

where T_{initial} is the initial temperature of the cool water.

2. Calculate ΔH for Each Reaction.

- e. Graph the temperature versus time for each of the three reactions tested. Extrapolate the line back to find the theoretical instantaneous mixing temperature, T_{mix} , as you did above.
- f. Calculate the amount of heat evolved in each reaction, q_{rxn} , by assuming that all of the heat is absorbed by the solutions and the calorimeter:

$$q_{\text{rxn}} = -[\text{heat absorbed by solution} + \text{heat absorbed by calorimeter}]$$

$$q_{\text{rxn}} = -[(\text{grams of solution} \times \text{specific heat of solution} \times \Delta T_{\text{solution}}) + (C_{\text{calorimeter}} \times \Delta T_{\text{solution}})]$$

where $\Delta T_{\text{solution}} = (T_{\text{mix}} - T_{\text{initial}})$ for each reaction mixture. Assume that the density of the solutions is 1.03 g/mL , and that the specific heat of the solutions is the same as that of water, $4.18 \text{ J/(g}\cdot^{\circ}\text{C)}$.

- g. Calculate the value of the enthalpy change, ΔH , in terms of kJ/mole for each of the reactions.

3. Verify Hess's Law.

- h. Write net ionic equations for the three reactions involved. Show how you must arrange the first two equations to algebraically find the third.
- i. Calculate the value of ΔH for the third reaction from your ΔH values for the first two reactions using Hess's law.
- j. Find the percent difference between the calculated and measured values.

Disposal

The solutions can be flushed down the drain with a 20-fold excess of water. Consult the *Flinn Chemical Catalog/Reference Manual*, suggested disposal method #26b. See the appendix.

Discussion

Include your data, calculations and answers to the following questions in your laboratory report:

1. What is meant by calorimetry?
2. How does the graphical temperature analysis improve the accuracy of your data?
3. The equation used to find the heat evolved in each reaction is $q_{\text{rxn}} = -[(\text{grams of solution} \times \text{specific heat of solution} \times \Delta T_{\text{solution}}) + (C_{\text{calorimeter}} \times \Delta T_{\text{solution}})]$. What is the meaning of the negative sign in front of the bracket?
4. Do your values support Hess's law?
5. How could you modify the method to achieve greater accuracy?
6. Find a table listing standard heats of formation for the species included in your net ionic equations. Use them to calculate ΔH for each of these net ionic equations. Do these values support Hess's law?